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L7: Entry 1 of 14

File: PGPB

Mar 7, 2002

DOCUMENT-IDENTIFIER: US 20020028361 A1

TITLE: Substrate with a photocatalytic coating

Summary of Invention Paragraph (24):

[0023] In an entirely surprising way, the coating exhibits in fact not one property but two, as soon as it is exposed to appropriate radiation, as in the visible and/or ultraviolet field, such as sunlight: by the presence of photocatalytic titanium oxide, as already seen, it promotes the gradual disappearance, as they are accumulated, of dirty marks of organic origin, their degradation being caused by a radical oxidation process. Inorganic dirty marks are not, themselves, degraded by this process: they therefore remain on the surface and, except for a degree of crystallization, they are in part easily removed since they no longer have any reason to adhere to the surface, the binding organic agents being degraded by photocatalysis.

## CLAIMS:

1. Glass-, ceramic- or vitroc ceramic-based substrate (1) , provided on at least part of at least one of its faces with a coating (3) with a photocatalytic property with a thickness between 5 and 50 nanometers and containing at least partially crystalline titanium oxide obtained by a pyrolysis technics from at least one precursor, notably an organo-metallic or a metallic halide component.
2. Substrate (1) according to claim 1, characterized in that the crystalline titanium oxide is in the anatase form, in the rutile form or in the form of a mixture of anatase and rutile.
3. Substrate (1) according to claim 1 or claim 2, characterized in that the titanium oxide is crystalline with a degree of crystallization of at least 25%, in particular of between 30 and 80%.
4. Substrate (1) according to one of the preceding claims, characterized in that the crystalline titanium oxide is in the form of crystallites with an average size of between 0.5 and 60 nm, preferably to 50 nm, in particular 10 to 40 nm.
5. Substrate (1) according to one of the preceding claims, characterized in that the coating (3) also contains an inorganic material, in particular in the form of an amorphous or partially crystalline oxide or mixture of oxides of the silicon oxide, titanium oxide, tin oxide, zirconium oxide or aluminium oxide type.
6. Substrate (1) according to one of the preceding claims, characterized in that the coating comprises additives capable of accentuating the photocatalytic phenomenon due to the titanium oxide, in particular by increasing the absorption band of the coating and/or by increasing the number of charge carriers by doping the crystal lattice of the oxide or by surface doping the coating and/or by increasing the yield and kinetics of the photocatalytic reactions by covering at least part of the coating with a catalyst.

7. Substrate (1) according to claim 6, characterized in that the crystal lattice of the titanium oxide is doped, in particular by at least one of the metal elements from the group comprising niobium, tantalum, iron, bismuth, cobalt, nickel, copper, ruthenium, cerium and molybdenum.

8. Substrate (1) according to claim 6, characterized in that the titanium oxide or the coating (3) in its entirety is coated with a catalyst, in particular in the form of a thin layer of noble metal of the platinum, rhodium, silver or palladium type.

10. Substrate (1) according to claim 6, characterized in that the surface doping of the titanium oxide or of the coating which contains it is carried out by covering at least part of the said coating with a layer of metal oxide or salts, the metal being chosen from iron, copper, ruthenium, cerium, molybdenum, bismuth or vanadium.

13. Substrate (1) according to one of the preceding claims, characterized in that at least one thin layer (2) with an anti-static, thermal or optical function or forming a barrier to the migration of the alkali metals originating from the substrate (1) is arranged under the coating (3) with a photocatalytic property.

20. Process for obtaining the substrate (1) according to one of claims 1 to 17, characterized in that the coating (3) with a photocatalytic property is deposited by liquid phase pyrolysis, in particular from a solution comprising at least one organometallic titanium precursor of the titanium chelate and/or titanium alcoholate type.

21. Process for obtaining the substrate (1) according to one of claims 1 to 17, characterized in that the coating (3) with a photocatalytic property is deposited by a sol-gel technique, with a method of deposition of the dipping or dip coating, cell coating, spray coating or laminar coating type, from a solution comprising at least one organometallic titanium precursor of the titanium alcoholate type.

22. Process for obtaining the substrate (1) according to one of claims 1 to 17, characterized in that the coating (3) with a photocatalytic property is deposited by vapour phase pyrolysis, CVD, from at least one titanium precursor of the halide or organometallic type.

23. Process according to one of claims 20 to 22, characterized in that the coating (3) with a photocatalytic property is deposited in at least two successive stages.

24. Process according to one of claims 20 to 23, characterized in that the coating (3) with a photocatalytic property is subjected, after deposition, to a least one heat treatment of the annealing type.

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## ☐ 2. Document ID: US 20020006865 A1

L7: Entry 2 of 14

File: PGPB

Jan 17, 2002

DOCUMENT-IDENTIFIER: US 20020006865 A1

TITLE: Photocatalytic substance

### Summary of Invention Paragraph (4):

[0004] The use of titanium oxide as a photocatalytic substance is known conventionally, and its use in various fields is being studied. In known photocatalysts using titanium oxide, catalytic function is observed under exposure to ultraviolet light with a wavelength shorter than 410 nm, but is not observed under visible light with a longer wavelength. Only about 5% of sunlight, falls in the

ultraviolet light range, so that known titanium oxide-based photocatalysts do not exhibit a sufficient catalytic function under sunlight. Thus, an ultraviolet light source, such as a mercury lamp, is sometimes separately provided to irradiate ultraviolet light on the photocatalyst in order to exhibit sufficient photocatalytic function.

**CLAIMS:**

1. A photocatalytic substance, comprising: a porous material; and a photocatalytic material comprising  $MOaXb$ , wherein M is metal, O is an oxygen, X is any element,  $a=1.5$  to  $2.0$ , and  $b=0.01$  to  $0.5$ , supported on the porous material and which operates when exposed to visible light.
2. The photocatalytic substance according to claim 1, wherein: said M is at least one of Ti, Sn, and Zn; and said X is at least one of N, S, P, B, C, Cl, As, Se, Br, Sb, Te, and I.
3. The photocatalytic substance according to claim 1, wherein said X has a chemical bond with said M.
4. The photocatalytic substance according to claim 1, wherein: said M is Ti; and at least one of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Re, Os, Ir, Pt, Mo, and Nb is contained by substituting at a titanium site of a Ti--O--X crystal, doping between Ti--O--X crystal lattices, doping to a crystalline grain boundary of Ti--O--X, or a combination of these.
5. The photocatalytic substance according to claim 1, wherein said porous medium is formed of alumina, silica, zirconia, titanium oxide, activated carbon, a mixture thereof or a composite thereof.
6. The photocatalytic substance according to claim 1, wherein said porous medium has mesopores.
7. The photocatalytic substance according to claim 6, wherein said porous medium has a honeycomb structure.
8. The photocatalytic substance according to claim 7, wherein said porous medium is formed on a substrate.
9. The photocatalytic substance according to claim 8, wherein said pores of said porous medium are oriented in a direction perpendicular to a surface of the substrate.

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### ☐ 3. Document ID: US 20020005145 A1

L7: Entry 3 of 14

File: PGPB

Jan 17, 2002

DOCUMENT-IDENTIFIER: US 20020005145 A1

TITLE: Nanoparticulate titanium dioxide coatings, and processes for the production and use thereof

Summary of Invention Paragraph (40):

[0040] Photocatalytic titanium oxides have been the focus of several efforts to introduce antifouling properties to coatings and masonry. Examples include Japanese Patent 11 228 204 "Cement composition containing photocatalyst and construction method using it"; Japanese Patent 11 061 042 "Highly hydrophilic inorganic coatings, coated

products therefrom and their uses"; and European Patent EP-A885 857 "Use of a mixture of organic additives for the preparation of cementitious compositions with constant color, and dry premixes and cementitious compositions containing the mixture". Wide-spread commercial use has been limited largely due to the relatively high cost and poor dispersion characteristics of commercially available photocatalytic titanium oxide powders. Using photocatalytic titanium oxide is attractive for an anti-fouling product because titanium oxides exhibit robust weatherability and low toxicity. The anatase crystalline form of titanium dioxide exhibits high photocatalytic activity and has been the most widely explored. A problem has been to introduce enough anatase titanium dioxide into the coating or surface formulation to impart anti-fouling properties while maintaining an economic advantage over commercially available leaching-type biocides.

Summary of Invention Paragraph (47):

[0047] The present invention still further contemplates highly photocatalytic aggregate particles comprised of an extender particle with discrete photocatalytic titanium oxide particles exposed on the surface. The aggregates may be used as additives for making non-toxic, antifouling coatings and building materials. This invention also includes building materials containing these aggregates and processes for making the aggregates and slurries of the aggregates.

Summary of Invention Paragraph (111):

[0111] In still yet another of its aspects, the present invention contemplates highly photocatalytic aggregate particles comprised of an extender particle with discrete photocatalytic titanium oxide particles exposed on the surface. The extender particle reduces the amount of premium photocatalyst required to achieve desired photocatalytic activity in a finished product. The discrete nature of the photocatalytic titanium oxide particles, applied in sufficient number, increases the photoactivity of the aggregate particles by increasing their photoactive surface area verses the surface area provided by a relatively flat continuous coating. The aggregates of this invention exhibit an inhibitory effect on surface-borne microorganisms when the mixtures are incorporated into building materials such as masonry, roofing shingles, siding, and antifouling coatings. Further, the aggregate particles show improved handling and dispersion in coating preparations versus virgin photocatalyst.

Summary of Invention Paragraph (114):

[0114] The preferred aggregate particles of the present invention--generally comprised of an extender particle with discrete photocatalytic titanium oxide particles exposed on the surface, which exhibit antifouling properties and improved dispersion in slurries and coatings--consist essentially of photocatalytic titanium oxide, preferably titanium dioxide in the anatase crystalline form, at less than about 20% by weight, preferably less than 10% by weight, and more preferably less than 6% by weight, and an extender particle at greater than 20% by weight. Preferred extender particles include silicate and carbonate powders, mineral and mineral composites including calcined clay and wollastonite, metal oxides including zinc oxide, inorganic pigments, and construction aggregates including roofing granules.

Detail Description Paragraph (103):

[0230] The photocatalytic titanium oxide is exposed on the surface of the extender particle in the form of discrete particles. The discrete particles may form small agglomerates, such as flocculated particles, on the surface of the aggregate particle, but this is less desirable because some discrete particles will then be shaded. The discrete particles typically have an average size within the range of 1 nanometer to 100 nanometers, preferably about 1 nanometers to 50 nanometers, and more preferably about 1 nanometers to 10 nanometers. The discrete particles can be observed and measured by electron microscopy such as scanning electron microscopy.

CLAIMS:

36. A composite body exhibiting a photocatalytic effect consisting essentially of a core particle consisting essentially of a material without deleterious effect on a photocatalytic reaction; and a multiplicity of nanoparticles, each less than 33% the diameter of the core particles, of photocatalytic material upon the surface of the core particle, the photocatalytic material being less than 20% by weight of (i) the combined multiplicity of photocatalytic material nanoparticles and (ii) the core

particle.

38. The composite body according to claim 36 wherein the core particle's material without deleterious effect on a photocatalytic reaction consists essentially of a material drawn from the group consisting essentially of silicates and carbonates including silicate and carbonate powders, mineral and mineral composites including calcined clay and wollastonite, metal oxides including zinc oxide, inorganic pigments, and construction aggregates including roofing granules.

42. The composite body according to claim 36 wherein the photocatalytic material of the multiplicity of nanoparticles is drawn from the group of metal compound semiconductors consisting essentially of titanium, zinc, tungsten and iron, and oxides of titanium, zinc, tungsten and iron, and strontium titanates.

43. The composite body according to claim 42 wherein the metal compound semiconductor photocatalytic material is combined with a metal or metal compound drawn from the group consisting of vanadium, iron, cobalt, nickel, copper, zinc, ruthenium, rhodium, silicon, tin, palladium, gold, platinum, and silver.

44. The composite body according to claim 36 wherein the photocatalytic material is drawn from the group of metal compound semiconductors consisting essentially of anatase titanium dioxide and zinc oxide.

45. The composite body according to claim 36 wherein the photocatalytic material consists of particles of a diameter from 1 nanometer to 100 nanometers.

46. The composite body according to claim 36 wherein the photocatalytic material consists of particles of diameter from 1 nanometer to 50 nanometers.

47. The composite body according to claim 36 wherein the photocatalytic material consists of particles of diameter from 1 nanometer to 10 nanometers.

49. The composite body according to claim 36 wherein weight of the photocatalytic material of the combined multiplicity of nanoparticles is less than 10% of weight of the core particle.

54. The composite body according to claim 36 wherein, at a proportion by weight of the photocatalytic material in the composite particle of less than 10%, the efficacy of the photocatalytic material within the composite particle to kill by contact algae, bacteria, mold, and fungus upon the composite particle's surface is at least one-half (0.5) as good as is the efficacy of this same photocatalytic material to kill in purest form, making that at least equal killing effect is realized with a five to one (5:1) reduction in the amount of photocatalytic material when this photocatalytic material is upon the surface of the composite particle.

55. A method of making composite photocatalytic particles comprising: preparing an aqueous slurry of first particles, consisting essentially of a material without deleterious effect on photocatalytic reaction, having an associated first particle size in the range from 100 nanometers to 1 centimeter diameter; adding a colloidal suspension of 0.1% to 60% by weight second particles, which second particles consist essentially of photocatalytic material having diameters in the range from 1 to 100 nanometers, the combined weight of second particles in the colloidal suspension being less than 20% of the combined weight of the first particles that are also within the aqueous slurry; mixing the aqueous slurry and the colloidal suspension so that the photocatalytic material second particles attach through van der Waals or fusion chemical forces to the nondeleterious material first particles, forming a slurry of composite particles wherein the relatively smaller photocatalytic material second particles (i) are upon the surfaces of the relatively larger nondeleterious material first particles, and (ii) are in weight less than 20% of these first particles.

58. The method according to claim 56 further comprising: adjusting the pH of the mixing so as to move away from, in the same direction, the respective isoelectric points of the photocatalytic material second particles and the nondeleterious material first particles, the isoelectric points being those points at which the particles have a neutral net charge.

59. The method according to claim 56 further comprising: adjusting the pH of the mixing so that either the photocatalytic material second particles or the nondeleterious material first particles approach their respective isoelectric points, but only when the mixture of both particles have low ionic strength and the pH is such that both particles are above or below their isoelectric points.
60. The method according to claim 56 further comprising: establishing an opposite electrical charge on the nondeleterious material first particles and the photocatalytic material second particles.
62. The method according to claim 56 further comprising one or more finishing steps drawn from the group consisting of separating, washing and drying the composite photocatalytic particles.
63. The method according to claim 56 further comprising drying the slurry of composite photocatalytic particles; and annealing in a kiln the dried composite photocatalytic particles.
64. The method according to claim 63 that, after the annealing, further comprises: rapidly cooling the annealed composite photocatalytic particles to ambient room temperature within a time period, which time period is necessarily dependent upon the temperature of the annealing and the amount of the composite photocatalytic particles, that is less than six hours.
65. The method according to claim 64 wherein the rapid cooling of the annealed composite photocatalytic is accomplished by rapid removal of the material from the kiln to a room temperature environment.
66. A photocatalytic aggregate particle consisting essentially of an extender particle of material both non-photocatalytic and non-interfering with photocatalytic reaction; with discrete photocatalytic titanium oxide particles exposed on the surface.
67. The photocatalytic aggregate particle according to claim 66 wherein the photocatalytic titanium oxide particles consists essentially of titanium dioxide in the anatase crystalline form.
68. The photocatalytic aggregate particle according to claim 66 wherein the photocatalytic titanium oxide particles are less than about 20% by weight.
69. The photocatalytic aggregate particle according to claim 66 wherein the extender particle is a material drawn from the group consisting essentially of silicates and carbonates including silicate and carbonate powders, mineral and mineral composites including calcined clay and wollastonite, metal oxides including zinc oxide, inorganic pigments, and construction aggregates including roofing granules.
70. A process of making photocatalytic aggregate particles comprising: mixing an aqueous slurry of extender particles made from material both nonphotocatalytic and non-interfering with photocatalytic reactions with a solution of titanyl sulfate; then adding an acid or an alkaline reacting agent to cause discrete microparticles of titanium dioxide to be deposited onto the extender particles.
71. A process for making photocatalytic aggregate particles comprising: mixing an aqueous slurry of extender particles made from material both nonphotocatalytic and non-interfering with photocatalytic reactions with an alkaline or acidic titania sol containing particles of titanium dioxide.
72. The process for making photocatalytic aggregate particles according to claim 71 wherein the titanium dioxide particles in the titania sol have an average diameter size within the range of about 1 to about 100 nanometers.
73. The process for making photocatalytic aggregate particles according to claim 71 wherein the titanium dioxide particles in the titania sol and the extender particles are both above or below their respective isoelectric points.

74. The process for making photocatalytic aggregate particles according to claim 71 wherein discrete particles of the titanium dioxide that is within the titania sol are dispersed onto the surfaces of the extender particles in an amount less than 20 weight % based on aggregate particle weight.

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#### 4. Document ID: US 20010040716 A1

L7: Entry 4 of 14

File: PGPB

Nov 15, 2001

DOCUMENT-IDENTIFIER: US 20010040716 A1

TITLE: Photocatalytic colored member and method of manufacturing the same

#### Detail Description Paragraph (22):

[0059] To wit, according to the present invention, the photocatalytic material is not dispersed in raw materials, but rather it consists solely of photocatalytic material, and moreover the photocatalytic material is made into thin films separated by vacant layers, thus giving a multi-layer film structure for photocatalytic material having fine grooves. Moreover, by adopting such a structure, since the pure material of titanium oxide which is the photocatalytic material is colorless and transparent, exhibiting a white color in powder form, based on the light diffraction effects due to this structure, an additional effect is generated wherein coloring can be obtained due to interference colors.

#### CLAIMS:

1. A photocatalytic colored member comprising a laminate formed by laminating a plurality of thin-film layers of photocatalytic material and a plurality of thin-film layers of support material, with vacant layers formed such that they are open to the outside on the rear surface side of the thin-film layers of photocatalytic material.
2. The photocatalytic colored member according to claim 1, wherein said thin-film layers of photocatalytic material have openings and said vacant layers communicate with said openings.
3. The photocatalytic colored member according to claim 1, wherein said photocatalytic material is titanium dioxide.
4. The photocatalytic colored member according to claim 1, wherein said thin-film layers of support material are made of one material selected from the group consisting of metals with a melting point of 400.degree. C. or higher, semiconductors, or insulators.
5. The photocatalytic colored member according to claim 2, wherein said openings are shaped like parallel grooves.
6. The photocatalytic colored member according to claim 2, wherein said openings are circular, elliptical or polygonal.
7. The photocatalytic colored member according to claim 2, wherein the intervals between said openings are disposed uniformly on the surface.
8. The photocatalytic colored member according to claim 2, wherein the intervals between said openings are disposed nonuniformly on the surface.
9. The photocatalytic colored member according to claim 2 which is formed by providing, upon a portion or the entire surface of the substrate, laminates consisting

of said laminated thin-film layers of photocatalytic material and thin-film layers of support material which maintain said vacant layers by means of thin-film layers of support material formed at the center having a circular, elliptical or polygonal cross section.

10. The photocatalytic colored member according to claim 1, wherein the surface area of each layer of said laminated thin-film layers of photocatalytic material is equal.

11. The photocatalytic colored member according to claim 2, wherein the surface area of each layer of said laminated thin-film layers of photocatalytic material is equal.

12. The photocatalytic colored member according to claim 1, wherein the surface area of each layer of said laminated thin-film layers of photocatalytic material becomes larger when going from the surface toward the bottom layer.

13. The photocatalytic colored member according to claim 2, wherein the surface area of each layer of said laminated thin-film layers of photocatalytic material becomes larger when going from the surface toward the bottom layer.

14. The photocatalytic colored member according to claim 1, wherein the surface area of each layer of said laminated thin-film layers of photocatalytic material becomes smaller when going from the surface toward the bottom layer.

15. The photocatalytic colored member according to claim 2, wherein the surface area of each layer of said laminated thin-film layers of photocatalytic material becomes smaller when going from the surface toward the bottom layer.

16. The photocatalytic colored member according to claim 1, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

17. The photocatalytic colored member according to claim 2, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

18. The photocatalytic colored member according to claim 3, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

19. The photocatalytic colored member according to claim 4, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

20. The photocatalytic colored member according to claim 5, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

21. The photocatalytic colored member according to claim 6, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

22. The photocatalytic colored member according to claim 7, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

23. The photocatalytic colored member according to claim 8, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

24. The photocatalytic colored member according to claim 9, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

25. The photocatalytic colored member according to claim 10, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of



photocatalytic material.

26. The photocatalytic colored member according to claim 11, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

27. The photocatalytic colored member according to claim 12, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

28. The photocatalytic colored member according to claim 13, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

29. The photocatalytic colored member according to claim 14, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

30. The photocatalytic colored member according claim 15, wherein a film of titanium oxide with the anatase structure is used as the thin-film layers of photocatalytic material.

31. The photocatalytic colored member according to any of claim 1, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

32. The photocatalytic colored member according to any of claim 2, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

33. The photocatalytic colored member according to any of claim 3, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

34. The photocatalytic colored member according to any of claim 4, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

35. The photocatalytic colored member according to any of claim 5, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

36. The photocatalytic colored member according to any of claim 6, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

37. The photocatalytic colored member according to any of claim 7, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

38. The photocatalytic colored member according to any of claim 8, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

39. The photocatalytic colored member according to any of claim 9, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

40. The photocatalytic colored member according to any of claim 10, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

41. The photocatalytic colored member according to any of claim 11, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

42. The photocatalytic colored member according to any of claim 12, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

43. The photocatalytic colored member according to any of claim 13, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

44. The photocatalytic colored member according to any of claim 14, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

45. The photocatalytic colored member according to any of claim 15, wherein a film of titanium oxide with the amorphous structure is used as the thin-film layers of photocatalytic material.

46. A method of manufacturing a photocatalytic colored member comprising the steps of: laminating a plurality of layers of thin-film layers of photocatalytic material and thin-film layers of support material, forming a plurality of openings through a plurality of layers of the multi-layer film by means of physical dry etching with argon ions or the like, and next, using wet etching to remove excess support material to form, on the rear surface side of the thin-film layers of photocatalytic material, vacant layers that are open to the outside.

47. A method of manufacturing a photocatalytic colored member comprising the steps of: laminating a plurality of layers of thin-film layers of photocatalytic material and thin-film layers of support material, and using dry etching to form, on the rear surface side of the thin-film layers of photocatalytic material, vacant layers that are open to the outside, where as the raw material gas for dry etching, argon gas or oxygen gas as the gas that performs physical etching is used simultaneously with chlorine gas or hydrogen chloride gas as the gas that performs chemical etching.

48. The method of manufacturing a photocatalytic colored member according to claim 46, wherein said thin-film layers of photocatalytic material are made of titanium oxide, and the equivalent surface area is increased by etching the titanium oxide film on the surface with wet etching or dry etching.

49. The method of manufacturing a photocatalytic colored member according to claim 47, wherein said thin-film layers of photocatalytic material are made of titanium oxide, and the equivalent surface area is increased by etching the titanium oxide film on the surface with wet etching or dry etching.

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw Desc | Image |
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## ☐ 5. Document ID: US 20010002994 A1

L7: Entry 5 of 14

File: PGPB

Jun 7, 2001

DOCUMENT-IDENTIFIER: US 20010002994 A1

TITLE: Dental and orologic composition

### Abstract Paragraph (2):

(a) a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor;

### Abstract Paragraph (7):

(c) a liquid medium. Another embodiment of the present invention provides a dental and orologic composition, that includes a photocatalytic titanium oxide or a

photocatalytic titanium oxide precursor. Another embodiment of the present invention provides a dental and orologic composition, that includes a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor, and a liquid medium. The composition of the present invention is particularly suitable in dental and oral care, and other embodiments of the present invention provide methods of making and using the above-described compositions.

Summary of Invention Paragraph (2):

[0002] The present invention relates to a dental and orologic composition containing a photocatalytic titanium oxide, and to a method of forming a photocatalytic titanium oxide-containing film on the surface of a dental material in or not in the mouth. More preferably, the invention relates to a dental and orologic composition containing a photocatalytic titanium oxide, which is to be applied to dental materials including tooth crown restorative materials, dentures, denture bases, denture rebases, orthodontic bases, wires, bridges, mouth pieces, etc., to teeth, gums or oral mucous membranes, or to teeth having been restored with composite resin or coated with dental manicare, to thereby form a film of the composition on their surfaces. The film thus formed prevents the formation of biofilm, that is, dental plaque containing a large number of bacteria in the mouth, and prevents dental caries and periodontitis or prevents the promotion of such dental diseases. In addition, it prevents or retards the discoloration of teeth and dental materials to be caused by adhesion of cigarette tar or food deposits thereto, bleaches discolored teeth, and even prevents halitosis. The invention also relates to a method of forming such a photocatalytic titanium oxide-containing film on the surface of a dental material in or not in the mouth.

Summary of Invention Paragraph (7):

[0007] Recently, a coating material that contains a photocatalytic titanium oxide has been proposed. This coating material is applied to the surfaces of appliances, tiles glass articles and others to form thereon an antibacterial, antifogging, antisoiling or deodorizing film owing to the photocatalytic activity of the titanium oxide in the material.

Summary of Invention Paragraph (8):

[0008] A liquid coating composition for teeth is known for applying such a photocatalytic titanium oxide to dental materials, which composition is prepared by mixing a photocatalytic titanium oxide with methyl .alpha.-cyanoacrylate and a resin component such as polymethyl methacrylate or the like (JP-A-175923/1997.) The published specification discloses that dental caries can be prevented by coating teeth with the coating composition. However, methyl .alpha.-cyanoacrylate used in the coating composition is extremely rapidly polymerized and cured by the moisture in air or by water in the mouth. The coating composition must therefore be applied to teeth within an extremely short period of time, and the coating composition is handled only with difficulty. In addition, the coating composition may not be completely safe for dental use in the mouth, since the composition contains methyl .alpha.-cyanoacrylate. Another problem with the coating composition is that its adhesion durability to teeth is poor, and the film that results from the coating composition is often peeled from teeth.

Summary of Invention Paragraph (26):

[0026] (a) a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor;

Summary of Invention Paragraph (32):

[0032] Another embodiment of the present invention provides a dental and orologic composition, that includes a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor.

Summary of Invention Paragraph (33):

[0033] Another embodiment of the present invention provides a dental and orologic composition, that includes a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor, and a liquid medium.

Summary of Invention Paragraph (38):

[0038] drying the applied composition to form a photocatalytic titanium oxide-containing film on the surface; and

Summary of Invention Paragraph (42):

[0042] drying the applied composition to form a photocatalytic titanium oxide-containing film on the surface; and

Summary of Invention Paragraph (46):

[0046] drying the applied composition to form a photocatalytic titanium oxide-containing film on the surface; and

Summary of Invention Paragraph (50):

[0050] drying the applied composition to form a photocatalytic titanium oxide-containing film on the surface; and

Summary of Invention Paragraph (54):

[0054] drying or baking or drying and baking the applied composition to form a photocatalytic titanium oxide-containing film on the surface; and

Summary of Invention Paragraph (56):

[0056] Another embodiment of the present invention provides a method for producing a dental and orologic composition, which includes admixing a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor with the dental and orologic composition.

Summary of Invention Paragraph (59):

[0059] drying or baking or drying and baking the applied composition to form a photocatalytic titanium oxide-containing film on the surface.

Summary of Invention Paragraph (62):

[0062] (a) a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor;

Summary of Invention Paragraph (69):

[0069] The present inventors have continued to study the applicability of photocatalytic titanium oxide to dental use. The present inventors have found that a resin composition containing a photocatalytic anatase-type titanium dioxide, a (meth)acrylate monomer and a polymerization initiator is favorable to dental materials, and that, when the resin composite on is used in producing dental materials for dentures, denture rebases, orthodontic bases, denture restorative materials, mouth pieces, etc., or when it is applied to the surfaces of such dental materials and then exposed to light, then the smelly component having adsorbed or adhered to the dental materials in the mouth is decomposed to be odorless, and have already filed a patent application for the invention based on the findings (JP-A-273412/1998, the entire contents of which are hereby incorporated by reference).

Summary of Invention Paragraph (70):

[0070] The inventors have further studied, and, as a result, have found that a composition containing a photocatalytic titanium oxide or its precursor, at least one selected from a silicon compound such as an alkyl silicate or its hydrolyzed condensate, a silicone resin, a silicone resin precursor and silica, and a liquid medium is easily handleable and highly safe and has good film-forming ability on the surfaces of teeth and dental materials, like the dental resin composition disclosed in the above-mentioned JP-A-273412/1998, and that, when the composition is applied to the surfaces of teeth, dental materials or gums to form a film thereon and thereafter the thus-formed film is exposed to light, then the film acts to prevent the adhesion of dental plaque to the film-coated surfaces and to promote the destruction and removal of the dental plaque having adhered to the surfaces, thereby effectively preventing and curing oral diseases and dental diseases such as dental caries, gingivitis, periodontitis and other peridental diseases (pyorrhea alveolaris, etc.), stomatitis, etc.

Summary of Invention Paragraph (71):

[0071] In addition, the present inventors have found that a composition containing a photocatalytic titanium oxide and a liquid medium is also effective for preventing and curing such oral diseases and dental diseases, like the composition as above, and that, after the treatment with the composition for preventing and curing the diseases

followed by exposure to light, the excessive composition can be readily removed from the treated site through washing with water. Moreover, we have found that a composition containing a photocatalytic titanium oxide precursor and a liquid medium is also effective like the compositions mentioned above.

Summary of Invention Paragraph (73):

[0073] When any of the above-mentioned compositions is applied to the surfaces of dental materials not in the mouth, or when a photocatalytic titanium oxide sol or a photocatalytic titanium oxide precursor is applied thereto not in the mouth, and thereafter dried and/or baked, then a film containing photocatalytic titanium oxide and having the above-mentioned effects can be smoothly formed on the surfaces.

Summary of Invention Paragraph (76):

[0076] (a) a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor,

Summary of Invention Paragraph (80):

[0080] (2) The dental and orologic composition of above (1), wherein the ratio of the photocatalytic titanium oxide or photocatalytic titanium oxide precursor to at least one selected from the silicon compound (I), a hydrolyzate of the silicon compound (I), a silicone resin, a silicone resin precursor and silica falls between 20/1 and 1/100 in terms of the molar ratio of titanium atom/silicon atom.

Summary of Invention Paragraph (81):

[0081] (3) The dental and orologic composition of above (1) or (2), wherein the photocatalytic titanium oxide precursor is a titanium alkoxide, and the silicone resin precursor is a silane compound and/or a silazane.

Summary of Invention Paragraph (82):

[0082] (4) A dental and orologic composition containing a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor.

Summary of Invention Paragraph (83):

[0083] (5) A dental and orologic composition containing a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor, and a liquid medium.

Summary of Invention Paragraph (88):

[0088] (10) A method for preventing and curing oral diseases and dental diseases, which comprises applying the dental and orologic composition of any one of above (1) to (8) to the surfaces of teeth, gums, dental materials fitted in the mouth, and/or oral mucous membranes, then drying it to form a photocatalytic titanium oxide-containing film on the surf aces, and thereafter exposing the film to light.

Summary of Invention Paragraph (89):

[0089] (11) A method for preventing and removing halitosis, which comprises applying the dental and orologic composition of any one of above (1) to (8) to the surf aces of teeth, gums, dental materials fitted in the mouth, and/or oral mucous membranes, then drying it to form a photocatalytic titanium oxide-containing film on the surf aces, and thereafter exposing the film to light.

Summary of Invention Paragraph (90):

[0090] (12) A method for preventing and retarding the discoloration of teeth and dental materials, which comprises applying the dental and orologic composition of any one of above (1) to (8) to the surfaces of teeth, gums and/or dental materials fitted in the mouth, then drying it to form a photocatalytic titanium oxide-containing film on the surf aces, and thereafter exposing the film to light.

Summary of Invention Paragraph (91):

[0091] (13) A method for bleaching discolored teeth, which comprises applying the dental and orologic composition of any one of above (1) to (8) to the surfaces of teeth, gums and/or dental materials fitted in the mouth, then drying it to form a photocatalytic titanium oxide-containing film on the surfaces, and thereafter exposing the film to light.

Summary of Invention Paragraph (92):

[0092] (14) A method for treating dental materials, which comprises applying the dental and orologic composition of any one of above (1) to (8) to the surfaces of dental materials not in the mouth, then drying and/or baking it to form a photocatalytic titanium oxide-containing film on the surf aces of the dental materials, and thereafter exposing the film to light.

Summary of Invention Paragraph (94):

[0094] (16) Use of a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor for producing a dental and orologic composition.

Summary of Invention Paragraph (95):

[0095] (17) Use of a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor, and a liquid medium for producing a dental and orologic composition.

Summary of Invention Paragraph (97):

[0097] (a) a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor,

Summary of Invention Paragraph (102):

[0102] The photocatalytic titanium oxide in the dental and orologic composition of the invention is preferably titanium oxide which, when exposed to light, exhibits photocatalytic activity to promote the decomposition of organic matters, nitrogen oxides, etc. More preferably the photocatalytic titanium oxide is anatase-type titanium dioxide.

Summary of Invention Paragraph (103):

[0103] Depending on the morphology of the photocatalytic titanium oxide therein, the dental and orologic composition of the invention is preferably grouped into the following compositions (A) and (B):

Summary of Invention Paragraph (104):

[0104] The dental and orologic composition of this type contains, as the component (a), a solid photocatalytic titanium oxide that exhibits photocatalytic activity by itself.

Summary of Invention Paragraph (105):

[0105] Preferably, the dental and orologic composition (A) contains (a) a photocatalytic titanium oxide, (b) at least one selected from a silicon compound of above formula (1), a hydrolyzate of the silicon compound (1), a silicone resin, a silicone resin precursor and silica, and (c) a liquid medium; or contains (a) a photocatalytic titanium oxide and (c) a liquid medium.

Summary of Invention Paragraph (106):

[0106] The dental and orologic composition of this type contains, as the component (a), a photocatalytic titanium oxide precursor.

Summary of Invention Paragraph (107):

[0107] Preferably, the dental and orologic composition (B) contains (a) a photocatalytic titanium oxide precursor, (b) at least one selected from a silicon compound of formula (I), a hydrolyzate of the silicon compound (1), a silicone resin, a silicone resin precursor and silica, and (c) a liquid medium or contains (a) a photocatalytic titanium oxide precursor and (c) a liquid medium.

Summary of Invention Paragraph (109):

[0109] The photocatalytic titanium oxide in the composition (A) is preferably in the form of particles (fine powder) having a mean particle size of from 0.001 to 0.5  $\mu\text{m}$ , more preferably from 0.005 to 0.1  $\mu\text{m}$ , as it is highly dispersible not forming a sediment while stored or transported, and has high photocatalytic activity. These ranges include all values and subranges therebetween, including 0.0015, 0.002, 0.01, 0.05, 0.075, 0.25, 0.35 and 0.45  $\mu\text{m}$ . Photocatalytic titanium oxide particles having a smaller particle size ensure higher photocatalytic activity. Therefore, in case where the composition (A) containing fine photocatalytic titanium oxide particles is directly applied to a predetermined site in the mouth and then exposed to light therein, it does not require any strong UV rays. Any weak UV rays that are safe to human bodies will be enough for ensuring the photocatalytic activity of the titanium

oxide in the composition (A). Titanium oxide having been prepared in a low-temperature plasma process and therefore having especially high photocatalytic activity exhibits its photocatalytic activity even when exposed to visible rays of 400 nm or longer. For these reasons, the composition (A) of the type is preferable for use in the mouth.

Summary of Invention Paragraph (110):

[0110] The photocatalytic titanium oxide content of the composition (A) preferably falls between 0.05 and 40% by weight, more preferably between 0.1 and 20% by weight, in view of the dispersion stability of the ingredient, photocatalytic titanium oxide in the composition, the photocatalytic activity thereof, the easiness in applying the composition to substrates, and the strength of the coated film of the composition. These ranges include all values and subranges therebetween, including 0.07, 0.9, 1.1, 2, 5, 10, 15, 25, 30 and 35%.

Summary of Invention Paragraph (111):

[0111] Preferably, the photocatalytic titanium oxide precursor in the composition (B) includes titanium alkoxides, chelates, acetates, halides, and their hydrolyzates, and one or more of these may be present in the composition (B). Of these, especially preferred are titanium alkoxides and/or their hydrolyzates. Specific examples of titanium alkoxides are titanium tetraethoxide, titanium tetrabutoxide, titanium tetra-n-propoxide, titanium tetramethoxide, etc. One or more of these may be used. Some titanium oxide precursors such as titanium tetraethoxide and others are commercially available, for example, as titanium oxide sol, and such commercial products are also preferably used.

Detail Description Paragraph (1):

[0117] (A-1) Composition containing photocatalytic titanium oxide particles, and a tetraalkoxysilane or its hydrolyzate in a liquid medium.

Detail Description Paragraph (2):

[0118] (A-2) Composition containing photocatalytic titanium oxide particles, and a silicone resin in a liquid medium

Detail Description Paragraph (3):

[0119] (A-3) Composition containing photocatalytic titanium oxide particles, and a silicone resin precursor such as an organosilane or its hydrolyzate, organosilazane or the like, in a liquid medium.

Detail Description Paragraph (4):

[0120] (A-4) Composition (suspension) containing photocatalytic titanium oxide particles and silica in a liquid medium.

Detail Description Paragraph (5):

[0121] (A-5) Composition containing a photocatalytic titanium oxide in a liquid medium.

Detail Description Paragraph (6):

[0122] (B-1): Composition containing a photocatalytic titanium oxide precursor such as a titanium tetraalkoxide or the like, and a tetraalkoxysilane or its hydrolyzate in a liquid medium.

Detail Description Paragraph (7):

[0123] (B-2) Composition containing a photocatalytic titanium oxide precursor such as a titanium tetraalkoxide or the like, and a silicone resin in a liquid medium.

Detail Description Paragraph (8):

[0124] (B-3): Composition containing a photocatalytic titanium oxide precursor such as a titanium tetraalkoxide or the like, and a silicone resin precursor such as an organosilane or its hydrolyzate, an organosilazane or the like, in a liquid medium.

Detail Description Paragraph (9):

[0125] (B-4): Composition containing a photocatalytic titanium oxide precursor such as a titanium tetraalkoxide or the like, and silica in a liquid medium.

Detail Description Paragraph (10):

[0126] (B-5): Composition containing a photocatalytic titanium oxide precursor such as a titanium tetraalkoxide or the like, in a liquid medium.

Detail Description Paragraph (15):

[0131] In the dental and orologic composition of the invention, the ratio of the photocatalytic titanium oxide or photocatalytic titanium oxide precursor to at least one selected from a silicon compound (I), a hydrolyzate of the silicon compound (I), a silicone resin, a silicone resin precursor and silica preferably falls between 20/1 and 1/100 in terms of the molar ratio of titanium atom/silicon atom, as the effect of the composition to decompose dental plaque and to retard the formation of dental plaque is high. More preferably, the ratio falls between 10/1 and 1/20. These ranges include all values and subranges therebetween, including 18/1, 15/1, 9/1, 5/1, 2/1, 1/1, 1/10, 1/25, 1/30, 1/40, 1/50, 1/70, 1/85 and 1/90.

Detail Description Paragraph (17):

[0133] The dental and orologic composition of the invention may be in any form of dilute solutions, dilute dispersions, highly viscous solutions, highly viscous dispersions, pastes, shape-forming gels, etc., for which the type and the content of the photocatalytic titanium oxide or its precursor and at least one selected from silicon compounds (I), their hydrolyzates, silicone resins, silicone resin precursors and silica that constitute the composition shall be appropriately selected and controlled.

Detail Description Paragraph (23):

[0139] For example, the composition (A) that contains photocatalytic titanium oxide particles may be applied to them according to the following methods:

Detail Description Paragraph (24):

[0140] (1) The composition (A) is applied to any of teeth, gums, oral mucous membranes, dental materials (tooth crown restorative materials, dentures, denture bases, denture rebases, orthodontic bases, wires, bridges, mouth places, etc.) fitted in the mouth, or teeth having been restored with composite resin or coated with dental manicure, and then optionally dried by exposing it to a gaseous blow (preferably a flowing gas stream) at a temperature not causing damage to the mouth to thereby form a photocatalytic titanium oxide-containing film on the substrate, and thereafter the film is exposed to light to express the photocatalytic activity of the photocatalytic titanium oxide therein.

Detail Description Paragraph (25):

[0141] (2) The composition (A) is applied to any of dental materials (tooth crown restorative materials, dentures, denture bases, denture rebases, orthodontic bases, wires, bridges, mouth pieces, etc.) not in the mouth, and then optionally dried and/or heated to thereby form a photocatalytic titanium oxide-containing film on the surface of the dental material, thereafter the film is exposed to light to express the photocatalytic activity of the photocatalytic titanium oxide therein, and the film-coated dental material is fitted into the mouth.

Detail Description Paragraph (26):

[0142] In the method (2), the steps of applying the composition (A) to the substrate, drying and heating it and then exposing it to light are all effected not in the mouth. In this, therefore, the composition (A) having been applied to the dental material may be dried and subjected to polycondensation at high temperatures, for example, at above 100.degree. C. Such high-temperature treatment is preferable for ensuring the formation of a tight and abrasion-resistant film that contains the photocatalytic titanium oxide and silica, on the surface of the dental material.

Detail Description Paragraph (28):

[0144] In order to convert a photocatalytic titanium oxide precursor such as a titanium alkoxide or the like into the corresponding photocatalytic titanium oxide (anatase-type titanium dioxide) having photocatalytic activity, it is necessary to bake the precursor at a temperature generally falling between 400 and 500.degree. C. These ranges include all values and subranges therebetween, including 410, 420, 430, 440, 450, 460, 470, 480 and 490.degree. C. Therefore, in case where the composition (B) is applied to dental materials to form thereon a film having photocatalytic activity, the dental materials must bear heating at the baking temperature. For such



heat-resistant dental materials, for example, used are castable ceramics, dental porcelains and metals. A preferred method employable for the composition (B) includes applying the composition (B) to a heat-resistant dental material of, for example, castable ceramics, dental porcelains or metals (e. g., crowns, inlays, bridges, dentures, metal bases, wires, clasps, brackets, etc. ), then optionally drying it, thereafter baking it at 400 to 500.degree. C. to thereby convert the photocatalytic titanium oxide precursor to the corresponding photocatalytic titanium oxide and to form a film that contains the thus-converted photocatalytic titanium oxide, on the dental material, and then exposing the film to light to express the photocatalytic activity of the photocatalytic titanium oxide, and finally fitting the thus-coated dental material to a predetermined site in the mouth.

Detail Description Paragraph (29):

[0145] In place of using the composition (B) that contains a photocatalytic titanium oxide precursor along with the component (b) (selected from silicon compounds (I), their hydrolyzates, silicone resins, silicone resin precursors and/or silica), a solution or dispersion (including titanium oxide sol, etc.) that contains a photocatalytic titanium oxide precursor but does not contain the component (b) is also usable in the invention to attain the same result specifically, in case where such a solution or dispersion is applied to a heat-resistant dental material not in the mouth, then baked at 400 to 500.degree. C. and thereafter exposed to light in the same manner as above, a film is formed on the dental material. Also in this case, the film formed on the dental material has photocatalytic activity, and the cured film thereon is effective for decomposing and removing dental plaque, for inhibiting dental plaque from adhering to the dental material, for preventing the dental material from being discolored and for preventing and removing halitosis. To that effect, the invention also encompasses the method of this case.

Detail Description Paragraph (30):

[0146] The photocatalytic activity of the photocatalytic titanium oxide-containing film that has been formed on the substrate of, for example, teeth, gums, oral mucous membranes, dental materials such as tooth crown restorative materials, dentures, denture bases, denture rebases, orthodontic bases, wires, bridges, mouth pieces, etc., and also teeth having been restored with composite resin or coated with dental manicure, is ensured to some degree even when the film is exposed to ordinary environmental light; however, in order to ensure higher photocatalytic activity of the film within a shorter period of time, it is preferable that the film is forcibly exposed to light by the use of a light emitter. In case where the photocatalytic activity of the film is lowered with the lapse of time, the film may be re-activated by exposing it to light. In particular, if the film is repeatedly exposed to light at regular intervals, it surely maintains its photocatalytic activity and is therefore extremely effective for inhibiting the deposition of dental plaque onto the surface of the film-coated substrate, for preventing the discoloration of the substrate, and for preventing halitosis. The method is especially preferable for detachable inlays, dentures, denture bases, cornus bridges, upper structures of implants, mouth pieces, etc.,. These coated with the film are detached and taken out of the mouth, and may be exposed to light outside of in the mouth.

Detail Description Paragraph (31):

[0147] The source of light to which the photocatalytic titanium oxide-containing film is exposed preferably includes an ordinary visible light emitter for dental use, dental light, and other engineering light emitters, and also mercury lamps, xenon lamps, metal halide lamps, halogen lamps, fluorescent lamps, sun light, etc. Depending on the mode of light emission from it and the site to be irradiated with it, a suitable light source shall be selected and used.

Detail Description Paragraph (32):

[0148] Preferably, a film that contains a photocatalytic titanium oxide is formed on the substrate of, for example, teeth, gums, oral mucous membranes, dental materials such as tooth crown restorative materials, dentures, denture bases, denture rebases, orthodontic bases, wires, bridges, mouthpieces, etc., as well as teeth having been restored with composite resin or coated with dental manicure, and the film is then exposed to light to thereby express the photocatalytic activity of the titanium oxide therein, whereby the dental plaque formed on the substrate is decomposed, or deposition of dental plaque onto the substrate is retarded. To that effect, the

photocatalytic titanium oxide-containing film formed on the substrate is effective for curing and preventing dental and oral diseases such as gingivitis, periodontitis and other peridental diseases (pyorrhea alveolaris, etc.), for preventing and retarding discoloration of teeth and dental materials, and for preventing and removing halitosis. In addition, the dental and orologic composition of the invention may be applied to discolored teeth in the same manner as described herein, to thereby decompose the discoloring component and bleach the discolored teeth.

Detail Description Paragraph (33):

[0149] In case where the composition of the invention is again applied to the oral mucous membranes, teeth, gums, dental materials, and composite resin-restored or dental manicure-coated teeth that have been once cleaned with the composition to remove the dental plaque therefrom, thereby forming the photocatalytic titanium oxide-containing film of the composition on them, it is possible to prevent redeposition of dental plaque onto these substrates. The durability of the photocatalytic titanium oxide-containing film in the mouth varies, depending on the site coated with the film, but, in general, the film can maintain its photocatalytic activity at least for a few days to a few weeks or so. Even when the photocatalytic activity of the film is lowered with the lapse of time, the film can be reactivated by again exposing it to light in the manner described hereinabove.

Detail Description Paragraph (36):

[0152] 2 parts by weight of tetraethoxysilane, 55 parts by weight of water and 35 parts by weight of ethanol were mixed by stirring them. The pH of the resulting mixture was controlled to fall between 1.5 and 2, and the tetraethoxysilane therein was hydrolyzed to prepare a uniform solution 8 parts by weight of photocatalytic titanium oxide particles (Ishihara Sangyo's ST-01, having a mean particle size of 0.007  $\mu$ m) were added thereto and uniformly dispersed to prepare a dental and orologic composition. This was a dilute dispersion, in which the molar ratio of titanium atom/silicon atom was 10/1.

Detail Description Paragraph (41):

[0157] The denture base on which the rebase had been polymerized and cured in the above (2)(ii) was taken out of water, and then left at room temperature for 1 day. Next, the dental and orologic composition that had been prepared in the above (1) was applied to the surface of the soft rebase of the denture base, and the liquid medium (water and ethanol) was evaporated away. Then, this was dried under heat at 90 to 100.degree. C. for 1 hour, and a photocatalytic titanium oxide-containing film was thus formed thereon. Next, the film was exposed to light from a dental light emitter (Morita's  $\alpha$ -Light) for 20 minutes to express the photocatalytic activity of the titanium oxide therein.

Detail Description Paragraph (43):

[0159] The denture base having been coated with the photocatalytic titanium oxide-containing film in the above (3) was fitted in the mouth of the patient, left as it was therein for 1 week and then taken out. The condition of the rebase of the denture base was macroscopically checked for plaque deposition thereon and for discoloration of the rebase. It was found that only slight plaque deposited on the surface of the rebase and that the rebase was not discolored. The plaque deposited on the surface of the rebase was readily removed by washing with water.

Detail Description Paragraph (44):

[0160] A denture base was coated with the same soft rebase as in the step (2)(ii) in Example 1. In this, however, the soft rebase was not coated with a photocatalytic titanium oxide-containing film. With that, the denture base was fitted in the mouth of the patient, left as it was therein for 1 week and then taken out. The condition of the rebase of the denture base was macroscopically checked for plaque deposition thereon and for discoloration of the rebase.

Detail Description Paragraph (47):

[0163] 2 parts by weight of tetraethoxysilane, 55 parts by weight of water and 35 parts by weight of ethanol were mixed by stirring them. The pH of the resulting mixture was controlled to fall between 1 and 2, and the tetraethoxysilane therein was hydrolyzed to prepare a uniform solution. 0.8 parts by weight of photocatalytic titanium oxide particles (Ishihara Sangyo's ST-01, having a mean particle size of

0.007 .mu.m) were added thereto and uniformly dispersed to prepare a dental and oralogic composition. This was a dilute dispersion, which had a photocatalytic titanium oxide content of 0.9% by weight and a tetraethoxysilane hydrolyzate content of 2.1% by weight and in which the molar ratio of titanium atom/silicon atom was 1/1.

Detail Description Paragraph (48):

[0164] (2) Formation of photocatalytic titanium oxide-containing film:

Detail Description Paragraph (50):

[0166] (ii) The dental and oralogic composition having been prepared in the previous step (1) was applied thin to the surface of the jacket crown prepared in (i), by the use of a brush, and the solvent was evaporated away. Then, this was heated at 150.degree. C. for 1 hour to thereby form a photocatalytic titanium oxide-containing film over the jacket crown (Example 2).

Detail Description Paragraph (53):

[0169] (i) The jacket crown (this was prepared in the previous step (2) (ii) and was coated with the photocatalytic titanium oxide-containing film) was fitted to the right-side, admaxillary central incisor of the anterior teeth of the patient, by the use of a dental resin cement (Kuraray's Panavia) In addition, the jacket crown (this was prepared in the previous step (2) (iii) and was not coated the photocatalytic titanium oxide-containing film) was fitted to the left-side, admaxillary central incisor of the anterior teeth of the patient, also by the use of the same dental resin cement as above.

Detail Description Paragraph (54):

[0170] (ii) After three months, the patient was recalled, and a plaque-staining liquid (Lion's Plaque Tester) was applied to its anterior teeth. With that, the surfaces of the jacket crowns were macroscopically checked for plaque deposition thereon. Little plaque deposition was seen on the jacket crown (this had the photocatalytic titanium oxide-containing film formed thereon) fitted to the right-side, admaxillary central incisor of the anterior teeth of the patient; but much plaque deposition was seen on and around the jacket crown (this did not have the photocatalytic titanium oxide-containing film) fitted to the right-side, admaxillary central incisor of the anterior teeth of the patient, from the cervical margin to the gingival margin and therearound.

Detail Description Paragraph (55):

[0171] (1) One part by weight of tetraethoxysilane, 2 parts by weight of titania sol (Ishihara Sangyo's STS-01) this is an aqueous sol that contains 30% by weight of titanium oxide having a mean particle size of 0.007 .mu.m), 70 parts by weight of ethanol and 2 parts by weight of water were mixed to prepare a dental and oralogic composition. This was a dilute liquid, which had a photocatalytic titanium oxide content of 0.8% by weight and a tetraethoxysilane content of 1.3% by weight and in which the molar ratio of titanium atom/silicon atom was 5/3.

Detail Description Paragraph (63):

[0179] (3) Three weeks after the treatment of the above (2), the treated part was stained with a plaque-staining liquid (Lion's Plaque Tester), and macroscopically checked for plaque deposition thereon. Plaque deposition on the site coated with the dental and oralogic paste was significantly smaller than that on the site not coated with it. In addition, a small amount of the tissue of the part coated with the dental and oralogic paste was collected and checked for deposition of bacteria of Streptococcus mutans and Candida albicans. Little deposition of the bacteria on the site was seen. The results confirm that the dental and oralogic composition that contains a photocatalytic titanium oxide and a silicon compound (i) along with fine silver particles is more effective for preventing and retarding dental plaque deposition and for killing bacteria.

Detail Description Paragraph (65):

[0181] (2) The metal-bonded porcelain bridge that had been prepared in the previous step (1) was sprayed thin with titanium oxide sol (Ishihara Sangyo's STS-01, having a titanium oxide content of 30% by weight), then dried, and baked at 500.degree. C. Thus, this was coated with photocatalytic titanium oxide (anatase-type titanium dioxide).

Detail Description Paragraph (71):

[0187] (1) 20 parts by weight of water, 40 parts by weight of glycerin, 10 parts by weight of the same photocatalytic titanium oxide powder as in Example 1, and 10 parts by weight of a silica fine powder (Aerosil 130) were mixed and uniformly dispersed to obtain a viscous dental and oralogic composition.

Detail Description Paragraph (74):

[0190] (1) A paste was prepared from 30 parts by weight of ethanol, 40 parts by weight of glycerin, 15 parts by weight of polyoxyethylene glycol having a mean molecular weight of about 400 and 15 parts by weight of polyoxyethylene glycol having a mean molecular weight of about 4000, in the same manner as in the step (1) in Example 7. In this, however, the paste prepared did not contain photocatalytic titanium oxide particles.

Detail Description Paragraph (82):

[0198] The dental and oralogic composition is capable of inhibiting dental plaque deposition and decomposing dental plaque to thereby prevent and cure dental diseases and oral diseases such as dental caries, gingivitis, periodontitis and other periodontal diseases (pyorrhea alveolaris, etc.), stomatitis, etc., and is effective for preventing discoloration of teeth and dental materials and for preventing and removing halitosis; and the composition is particularly suitable for dental and oral care. The dental and oralogic composition preferably contains a photocatalytic titanium oxide or its precursor; at least one selected from silicon compounds such as tetraalkoxysilanes, silicone resins and their precursors and silica, and a liquid medium; or it contains a photocatalytic titanium oxide or its precursor and a liquid medium. The method for oral and dental care includes applying the composition to teeth, gums, oral mucous membranes or dental materials in the mouth, or applying the composition to dental materials not in the mouth, to thereby fix photocatalytic titanium oxide on them or form a photocatalytic titanium oxide-containing film on them.

## CLAIMS:

1. A composition, comprising: (a) a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor; (b) at least one selected from the group consisting of: a silicon compound having the following formula (I):  $6\text{wherein } X^{\text{sup.1}}, X^{\text{sup.2}}, X^{\text{sup.3}}$  and  $X^{\text{sup.4}}$  each independently represent an alkoxy group or a halogen atom, a hydrolyzate of said silicon compound (I), a silicone resin, silicone resin precursor and silica; and (c) a liquid medium.

3. The composition as claimed in claim 1, wherein the photocatalytic titanium oxide precursor in (a) is a titanium alkoxide.

9. A dental and oralogic composition, comprising a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor.

10. A dental and oralogic composition, comprising a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor, and a liquid medium.

14. A method for preventing or curing oral diseases or dental diseases, which comprises: applying the composition as claimed in claim 1 to a surface of at least one selected from the group consisting of teeth, gums, dental materials fitted in the mouth, oral mucous membranes, dental materials not in the mouth, and combinations thereof, to form an applied composition; drying said applied composition to form a photocatalytic titanium oxide-containing film on said surface; and exposing said film to light.

15. A method for preventing or removing halitosis, which comprises: applying the composition as claimed in claim 1 to a surface of at least one selected from the group consisting of teeth, gums, dental materials fitted in the mouth, oral mucous membranes, dental materials not in the mouth, and combinations thereof, to form an applied composition; drying said applied composition to form a photocatalytic titanium oxide-containing film on said surface; and exposing said film to light.

16. A method for preventing or retarding the discoloration of teeth or dental materials, which comprises: applying the composition as claimed in claim 1 to a surface of at least one selected from the group consisting of teeth, gums, dental materials fitted in the mouth, oral mucous membranes, dental materials not in the mouth, and combinations thereof, to form an applied composition; drying said applied composition to form a photocatalytic titanium oxide-containing film on said surface; and exposing said film to light.
17. A method for bleaching discolored teeth, which comprises: applying the composition as claimed in claim 1 to a surface of at least one selected from the group consisting of teeth, gums, dental materials fitted in the mouth, oral mucous membranes, dental materials not in the mouth, and combinations thereof, to form an applied composition; drying said applied composition to form a photocatalytic titanium oxide-containing film on said surface; and exposing said film to light.
18. A method for treating dental materials, which comprises: applying the composition as claimed in claim 1 to a surface of a dental material, to form an applied composition; drying or baking or drying and baking said applied composition to form a photocatalytic titanium oxide-containing film on said surface; and exposing said film to light.
20. A method for producing a dental and orologic composition, comprising admixing a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor with said dental and orologic composition.
21. A film, produced by a process comprising: applying the composition as claimed in claim 1 to a surface, to form an applied composition; and drying or baking or drying and baking said applied composition to form a photocatalytic titanium oxide-containing film on said surface.
24. A method for preparing a dental and orologic composition, comprising admixing: (a) a photocatalytic titanium oxide or a photocatalytic titanium oxide precursor; (b) at least one selected from the group consisting of: a silicon compound having the following formula (I):  $\text{X}^{\text{sup.1}}\text{X}^{\text{sup.2}}\text{X}^{\text{sup.3}}\text{X}^{\text{sup.4}}$  wherein X.sup.1, X.sup.2, X.sup.3 and X.sup.4 each independently represent an alkoxy group or a halogen atom, a hydrolyzate of said silicon compound (I), a silicone resin, silicone resin precursor and silica; and (c) a liquid medium.

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | RWMC | Draw Desc | Image |
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## ☐ 6. Document ID: US 6326079 B1

L7: Entry 6 of 14

File: USPT

Dec 4, 2001

DOCUMENT-IDENTIFIER: US 6326079 B1  
 TITLE: Substrate with a photocatalytic coating

### Brief Summary Paragraph Right (20):

In an entirely surprising way, the coating exhibits in fact not one property but two, as soon as it is exposed to appropriate radiation, as in the visible and/or ultraviolet field, such as sunlight: by the presence of photocatalytic titanium oxide, as already seen, it promotes the gradual disappearance, as they are accumulated, of dirty marks of organic origin, their degradation being caused by a radical oxidation process. Inorganic dirty marks are not, themselves, degraded by this process: they therefore remain on the surface and, except for a degree of crystallization, they are in part easily removed since they no longer have any reason to adhere to the surface, the binding organic agents being degraded by photocatalysis.

## CLAIMS:

1. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and obtained by chemical vapor deposition followed by an annealing heat treatment.
2. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and obtained by liquid phase pyrolysis followed by an annealing heat treatment.
3. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and obtained by a sol gel technique followed by an annealing heat treatment.
13. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein the coating has a porosity of about 65 to 99%.
15. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein the coating has a refractive index between about 1.9 and 2.3.
16. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein the coating constitutes the final layer of a stack of anti-glare layers.
17. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein the coating is overlaid by an oleophobic and/or hydrophobic layer which is stable or resistant to photocatalysis.
19. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein at least one thin layer having an anti-static or optical function is located between said substrate and said coating.
22. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces, and contacting said portion, with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form.
23. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces, with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, and wherein an underlayer is present between, and contacts, said substrate and said coating, and which underlayer acts as a barrier with respect to alkali ions.
24. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces, with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form and at least one of an amorphous or partially crystalline oxide selected from the group consisting of oxides of silicon, titanium in other than anatase form, tin, zirconium and aluminum.
27. A double glass glazing comprising on at least a portion of one of its outer faces

a coating having photocatalytic properties, wherein said coating comprises titanium oxide at least partly crystallized in the anatase form.

28. An architectural material selected from the group consisting of facing material, cladding material and roofing material, and provided on at least a portion of one of its faces, with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form.

30. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces, and contacting said portion, with a hydrophilic coating having photocatalytic properties, and comprising at least partly crystallized titanium oxide.

31. A coated substrate which is a glass, ceramic or vitro-ceramic substrate provided on at least a portion of one of its faces with a coating having photocatalytic properties, and comprising titanium oxide at least partly crystallized in the anatase form, wherein the crystallized titanium oxide is in the form of crystallites, and the thickness of the coating is at least two times greater than the mean diameter of said crystallites.

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw Desc | Image |
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## 7. Document ID: US 6307620 B1

L7: Entry 7 of 14

File: USPT

Oct 23, 2001

DOCUMENT-IDENTIFIER: US 6307620 B1

TITLE: Substrate holding apparatus, substrate transfer system, exposure apparatus, coating apparatus, method for making a device, and method for cleaning a substrate holding section

### Detailed Description Paragraph Right (13):

FIG. 4 is a cross-sectional view of a second modification of the wafer chuck. In this modification, a titanium oxide photocatalytic thin-film 50c is provided at the tip of each pin which comes into contact with the wafer. This configuration also exhibits photocatalytic effects. When the photocatalytic thin-film is also formed on the peripheral region of the pin, the photocatalytic cleaning effects are further enhanced with respect to foreign materials primarily lying in the peripheral region.

### CLAIMS:

1. An exposure apparatus comprising:

a light source for emitting a light beam to expose a substrate; and

a substrate holding apparatus having a substrate holding section for holding a substrate, said substrate holding section including a thin film that causes a photocatalytic reaction upon irradiation with light,

wherein said light source irradiates said substrate holding section with the light beam.

4. An exposure apparatus according to claim 1, wherein the thin film comprises titanium oxide.

5. An exposure apparatus according to claim 4, wherein the titanium oxide is

heat-treated at 800.degree. C. or less.

29. A method of making a device comprising the steps of:

providing an exposure apparatus according to claim 1;

transferring a pattern formed in a reticle onto a wafer; and

exposing the substrate holding apparatus with light, causing a photocatalytic reaction.

31. A method of cleaning a substrate holding apparatus having a substrate holding section for holding a substrate, said method comprising the steps of:

providing the substrate holder with a thin film of separated segments, which causes a photocatalytic reaction upon irradiation with light;

moving the substrate holding section into an irradiation region of a light irradiation unit; and

irradiating the substrate holding section with light from the light irradiation unit.

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## ☐ 8. Document ID: US 6299981 B1

L7: Entry 8 of 14

File: USPT

Oct 9, 2001

DOCUMENT-IDENTIFIER: US 6299981 B1

TITLE: Substrate with improved hydrophilic or hydrophobic properties, comprising irregularities

### Brief Summary Paragraph Right (15):

According to an advantageous characteristic, the irregularities are created on the surface of the substrate by forming a textured coating in which they are due to particles of a photocatalytic agent, such as titanium dioxide  $\text{TiO}_2$ . In the absence of any hydrophobic/oleophobic treatment, such a coating, as soon as it is exposed to suitable radiation, such as visible light and/or ultraviolet radiation, has two interesting properties: the presence of photocatalytic titanium oxide, as already seen, promotes the gradual disappearance, progressively as they build up, of stains of organic origin by causing them to degrade by a radical oxidation process.

### CLAIMS:

9. The window glazing according to claim 1, wherein said relief is provided by a coating containing a photocatalytic agent.

10. The window glazing according to claim 9, wherein said photocatalytic agent is titanium oxide.

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## 9. Document ID: US 6242862 B1

L7: Entry 9 of 14

File: USPT

Jun 5, 2001

DOCUMENT-IDENTIFIER: US 6242862 B1

TITLE: Photocatalyzer and lamp or lighting fixture having a photocatalyzer

### Brief Summary Paragraph Right (13):

On the other hand, when the photocatalytic membrane is formed according to the so-called dipping method to attach a coating liquid to a base body by dipping it in a coating liquid containing such organic titanium compound as titanium alkoxide, titanium alkoxide and high boiling point organic compound causes hydrolysis with moisture in the air when pulling the base body out of the coating liquid. However, moisture does not readily arrive at the base body side and the hydrolysis at the base body side is insufficient and is not completely evaporated during the heating process at the time of calcination and is thermally cracked and scattered via such intermediate product as hydrocarbon. Therefore, it was revealed that impurities such as carbon increases in the photocatalytic membrane which tends to be reduced and titanium oxide in the photocatalytic membrane tends to become a rutile crystal that is partially inferior in the photocatalytic action. Thus the photocatalytic action of an obtained photocatalytic membrane tends to drop.

### Brief Summary Paragraph Right (29):

Because the photocatalytic membrane comprises mainly ultra fine particles of titanium oxide, its photocatalytic action is strong like a conventional photocatalytic membrane using ultra fine particles of titanium oxide. When a metallic oxide that has a refractive index smaller than that of the photocatalytic membrane, for instance, silicon oxide, aluminum oxide, is used as a metallic oxide for constituting the ground layer, the refractive index is decreased and the generation of light interference can be prevented. Thus, the light transmission factor of the photocatalytic membrane is improved and a transparent photocatalyzer is obtained.

### Brief Summary Paragraph Right (35):

One embodiment of the photocatalyzer of the present invention will now be described. First, a base body is provided. A porous ground layer made of metal oxide is formed on the base body. A photocatalytic membrane made of mainly ultra fine particles of titanium oxide is formed on the ground layer by closely fitting to the ground layer. "Porous" refers to the porosity being more than 30% and preferably below 70%. Porosity is continuous and may be continuous from the surface of the ground layer to the surface of the base body or continuous to the middle of the ground layer. If the porosity is in excess of 70%, the strength of the ground layer drops remarkably and it is therefore desirable to restrict it to below 70%. When the ground layer is porous, its surface also becomes uneven and it becomes easy for fine particles of titanium oxide of the photocatalytic membrane to enter into the uneven surface and closely fit thereto. When the ground layer is porous, it becomes easy to contain moisture and wettability is improved, and adhesion of the photocatalytic membrane is promoted.

### Brief Summary Paragraph Right (43):

When fine particles of titanium oxide are mixed with silicon oxide and baked, it is possible to have silicon oxide to act as a binder and form a ground layer that has a satisfactory adhesion to the base body. By using titanium oxide in average particle size larger than that of fine particles of titanium oxide of the photocatalytic membrane, for instance, 30.about.200 nm, an uneven surface of average depth 20.about.150 nm can be easily formed on the surface of the ground layer.

### Brief Summary Paragraph Right (55):

A desired metallic compound is added to a coating liquid containing titanium alkoxide. The liquid is used to coat the base body. The coated base body is then baked which generates titanium oxide and metallic oxide by hydrolyzing titanium compound and metallic compound contained in a coating liquid with moisture in the air and generate titanium oxide and metallic oxide is used. To change the content of metallic oxide in

the direction of membrane thickness, the decomposition of metallic compound is made faster than that of titanium compound and also, solubility is of hydrolyzed titanium and metal in the gel state into a solvent is reduced. Further, although the adding amount of metallic oxide somewhat varies according to which type of oxide and solvent are used, a proper amount is 10.about.50 wt % against titanium oxide in the photocatalytic membrane. If the adding amount is less than 10 wt %, the exudation preventive action of sodium is not sufficient and if exceeding 50 wt %, the visible rays transmission factor will drop.

CLAIMS:

1. A photocatalyzer comprising:

a base body;

a ground layer formed on the base body, the ground layer comprising a metallic oxide having an uneven surface; and

a photocatalytic membrane formed on the uneven surface of the ground layer, the membrane being made of mainly ultra fine particles of titanium oxide, formed by entering into portions of the uneven surface of the ground layer and being closely fitted thereto;

wherein the average depth of the uneven surface of the ground layer is larger than the average particle size of ultra fine particles of titanium oxide of the photocatalytic membrane.

2. A photocatalyzer as set forth in claim 1, wherein

the average depth of the uneven surface of the ground layer is 20 to 150 nm; and

the average particle size of ultra fine particles of titanium oxide of the photocatalytic membrane is 1 to 20 nm.

3. A photocatalyzer comprising:

a base body;

a ground layer formed on the base body, the ground layer comprising a metallic oxide having an uneven surface; and

a photocatalytic membrane formed on the uneven surface of the ground layer, the membrane being made of mainly ultra fine particles of titanium oxide, formed by entering into portions of the uneven surface of the ground layer and being closely fitted thereto;

wherein the ground layer has concave portions that penetrate to the surface of the base body, and a part of the photocatalytic membrane fills the concave portion.

4. A photocatalyzer comprising:

a base body;

a ground layer formed on the base body, the ground layer comprising a metallic oxide having an uneven surface; and

a photocatalytic membrane formed on the uneven surface of the ground layer, the membrane being made of mainly ultra fine particles of titanium oxide, formed by entering into portions of the uneven surface of the ground layer and being closely fitted thereto;

wherein the ground layer comprises a mixture of silicon oxide and titanium oxide mixed at a weight ratio 40:60 to 80:20.

5. A photocatalyzer comprising:

a base body, and

a photocatalyzer membrane formed on the base body such that the membrane has a base body side facing the base body and a surface side facing away from the base body, the membrane being made of a photocatalytic material comprising titanium oxides as a principal constituent mixed with metallic oxide, the metallic oxide content being greater on the base body side of the membrane than it is on the surface side.

| Full | Title | Citation | Front | Review | Classification | Date | Reference | Sequences | Attachments | Claims | KWIC | Draw Desc | Image |
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## ☐ 10. Document ID: US 6165256 A

L7: Entry 10 of 14

File: USPT

Dec 26, 2000

DOCUMENT-IDENTIFIER: US 6165256 A

TITLE: Photocatalytically hydrophilifiable coating composition

### Detailed Description Paragraph Right (112):

This demonstrates that addition of a surfactant in addition to photocatalytic titanium oxide particles, silica, and ethanol offers not only a permanent antifogging property but also an initial antifogging property.

### Detailed Description Paragraph Right (113):

The larger the amount of the surfactant, the longer the temporary loss time of the antifogging property. Specifically, for the sample prepared by coating the coating liquid sample B2 with the surfactant being added thereto in an amount as small as 0.4 part by weight based on one part by weight of the photocatalytic titanium oxide particle, the loss time was about 2 hr, and, for the sample prepared by coating the coating liquid sample B3 with the surfactant being added thereto in an amount of 1 part by weight, the loss time was about 5 hr, whereas for the sample prepared by coating the coating liquid sample B4 with the surfactant being added thereto in an amount of 2 parts, the loss time was about 24 hr. Further, for the sample prepared by coating the coating liquid sample with the surfactant being added thereto in an amount of 10 parts by weight based on one part by weight of the photocatalytic titanium oxide particles, the temporary loss time of the antifogging property was 200 hr or more.

### CLAIMS:

1. A composition for hydrophilifying the surface of a member, comprising at least

- (a) photocatalytic particles of a metallic oxide,
- (b) a silicon-based component selected from the group consisting of silica fine particles, a precursor capable of forming a silica film and combinations thereof, and
- (c) a solvent,

wherein the total content of the photocatalytic particles and the silicon in the silicon-based component in the composition is 0.01 to 1% by weight.

4. The composition according to any one of claims 1 to 3, wherein the average crystallite diameter of the photocatalytic particles is 100 nm or less.

5. The composition according to any one of claims 1 to 3, wherein the photocatalytic particles are constituted by the anatase form of titanium oxide.

9. The composition according to claim 8, wherein the content of the surfactant is less

than 10 parts by weight based on one part by weight of the photocatalytic particle.

10. The composition according to claim 9, wherein the content of the surfactant is 0.4 to 2 parts by weight based on one part by weight of the photocatalytic particle.

14. The composition according to any one of claims 1 to 3, wherein the photocatalytic oxide is selected from the group consisting of anatase form of titanium oxide, rutile form of titanium oxide, zinc oxide, tin oxide, ferric oxide, dibismuth trioxide, tungsten trioxide, and strontium titanate.

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